Maleic Anhydride Polyethylene Octene Elastomer Toughened Polyamide 6 / Polypropylene Nanocomposites: Mechanical And Morphological Properties

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A series of polyamide 6 / polypropylene (PA6/PP) blends containing 4 wt% of organophilic modified montmorillonite (MMT) were designed and prepared by melt compounding followed by injection moulding. Maleic anhydride polyethylene octene elastomer (POE-g-MA) was used as impact modifier as well as compatibilizer in the blend system. Three weight ratios of PA6/PP blends were prepared i.e. 80/20, 70/30, and 60/40. The mechanical properties of PA6/PP blends and nanocomposite were studied through flexural and impact properties. Scanning electron microscopy (SEM) was used to study the microstructure. The incorporation of 10wt% POE-g-MA into PA6/PP blends significantly increased the toughness with a corresponding reduction in strength and stiffness. However, on further addition of 4 wt% organoclay, the strength and modulus increased but with a sacrifice in impact strength. It was also found that the mechanical properties are a function of blend properties. Interesting, 70/30 PA6/PP blend ratio has the optimum impact strength values for both blends and nanocomposites. The morphological study revealed that POE-g particles were finely dispersed in the PA6 dominant blends system.

Key words: polyamide 6/polypropylene blends, polyethylene octene elastomer, mechanical properties, nanocomposites, toughened polymers

INTRODUCTION

In recent year, there has been much interest in the development of polymer blends based on engineering polymer such as polyamide (PA) with polypropylene (PP). Blending PA with PP leads to materials with improve chemical and moisture resistance, dimension stability and reduced cost [1-7]. However both polymers are immiscible and form heterogeneous systems due to different polarities between PA and PP. Much effect has been devoted to the compatibilization of the incompatibility PA6PP blends such as using PP-g-MA [1-3] or modified olefinic rubber [4-8].

Maleated rubbers such as EPR-g-MA, SEBS-g-MA, and EPDM-g-MA are known to act both as an impact modifier and compatibilizer for PA6/PP blends [4-8]. It is well recognized that maleic anhydride can react with the end groups of PA to form graft copolymer, which act as the compatibiliser that helps to disperse the co-continuous phase in the matrix phase and to strengthen the PA-PP interface.

Few years ago, polyethylene octene elastomer (POE) a metallocene elastomer have attracted considerable attention due to POE typically exhibit faster mixing and better dispersion when blended with PP compared with conventional polyolefin elastomer [7-8].

On the other hand, rubber toughening is accompanied by a reduction in a material strength and stiffness. The inclusion of rigid filler leads to compensate in stiffness and strength that sacrificed after incorporation of elastomeric materials. In recent year polymer nanocomposites based on layered clays have received increasing interest [1,3,6,10]. Nanocomposites exhibit superior properties such as enhanced stiffness and strength, reduced gas permeability and improved flame retardency.

The toughened PAPP and PAPP nanocomposites have been studied extensively by previous researchers on morphology, mechanical and processing. However, little work has been done on combination of toughened PA6PP and nanocomposites. This paper focus on the effectiveness of inclusion POE-g-MA and organoclay filler for different PA6PP weight ratio; 100:0, 80:20, 70:30, 60:40, 0:100)

MATERIALS AND METHODS

Materials

The blends used in this work are described in Table 1. The PA6 (Amilan CM 1017) was a commercial product from Toray Nylon Resin AMILAN, Japan. The MFI of PA6 is 35g/10 min at 230°C and 2.16 kg load and the density 1.14 g/cm^3. Polyethylene octene random (11wt% octene) copolymer grafted with maleic anhydride of DuPont (Fusabond MN493D) with density 0.87 g/cm^3 was used as impact modifier. Lastly, the organoclay (Nanomer 1.30TC) was a commercial product from Nanocor Inc. USA. This organoclay is a white powder containing montmorillonite (MMT) (70wt%) intercalated by octadecylamine (30wt%).

Table 1: Blends used in this work (wt%)

Formulation	*PA6 (Amilan CM 1017)*	*PP (SM 240)*	*Modified rubber (Fusabond MN493D)*	*Organoclay (Nanomer 1.30TC)*
Neat				
PA	100	-	-	-
PAPP (8:2)	80	20	-	-
PAPP (7:3)	70	30	-	-
PAPP (6:4)	60	40	-	-
PP	-	100	-	-
POE-g				
PAE10	90	-	10	-
PAPP (8:2)E10	72	18	10	-
PAPP (7:3)E10	63	27	10	-
PAPP (6:4)E10	54	36	10	-
PPE10	-	90	10	-
POE-g/organoclay				
PAE10FA4	86	-	10	4
PAPP (8:2)E10FA4	68.8	17.2	10	4
PAPP (7:3)E10FA4	60.2	25.8	10	4
PAPP (6:4)E10FA4	51.6	34.4	10	4
PPE10C6FA4	-	86	10	4

2.2 Specimen preparation

PA6, PP, POE-g and MMT were dry blended in tumbler mixer according to the composition in Table 1. The polymers and additives were then melt blended by simultaneous addition for all components into a Berstoff co-rotating twin screw extruder. The barrel temperatures were gradually increased from hopper to die at 200, 220, 230 and 240°C and the rotating screw was 50 rpm. Prior to extrusion, PA6 pellets were dehumidified by using a dryer at 80°C for 8 h. The pelletized materials were dried and injection molded into a standard specimen for mechanical tests.

2.3 Materials characterization

2.3.1 Mechanical Testing Flexural test were carried out according to ASTM D790 method using an Instron 5567 Universal Testing Machine under ambient condition. The crosshead speed for flexural test was set at 3 mm/min. The Izod impact test was carried out on notched specimens using Toyoseiki impact tester at ambient condition according to ASTM D256. In all cases, five specimens of each were tested and the average values were reported.

2.3.2 Microscopy examination (SEM): The morphology of the blends was examined using a Philips scanning electron microscope. Samples were cryogenically fractured in liquid nitrogen and etched in hot heptane for 5 hours to extract the elastomeric POE-g phase. Samples were coated with gold prior to examination under the electron beam. An operating voltage of 30kV and a magnification of 1000x were used.

RESULT AND DISCUSSION

Mechanical properties

Three types of samples were tested in this study that is pure, POE-g toughened and POE-g toughened nanocomposites PA6, PP and PA6/PP blends. Figure 1 and 2 shows the flexural strength and modulus as a function of weight fraction for all samples. It can be seen that flexural strength and modulus of all samples follow the same trend. The flexural strength and modulus of samples containing pure PA6 are higher compared to pure PP and decreased with increasing PP weight fraction. This may be attributed by the strength and stiffness of PA6 itself higher than of PP. A sharp drop strength and modulus is observed with the incorporation of 30 wt % PP, but the declines of properties were more gradual with further addition of PP. The results also show that the flexural strength and modulus were reduced with the incorporation of POE-g to the PA6, PP and PA6/PP blends. This trend generally found in various blends due to the softening or diluting effect of the materials with addition of elastomer [7]. The reduction of flexural strength and modulus was about 50% and 62% for the PA6/PP (70:30) blend respectively. However, interestingly the addition of organoclay into POE-g toughened samples enhanced the flexural strength and modulus of the POE-g toughened samples. The incorporation of organoclay in the blends leads to improve strength and modulus due to the stiffness of silicates layers contributes to the presence of immobilized or partially immobilized polymer phases [Liu PP, PA6]. Furthermore the high aspect ratio of organoclay resulting high contact surface with polymer matrix also contributes the improvement in modulus and strength. In addition of hydrogen bonding formed between organoclay and PA6 as well as organoclay with PA6-g-POE copolymer

As shown in Figure 3 the impact strength of PA6/PP blends was higher than pure PA6 and increased gradually with increasing PP weight fraction. According to Tseng et al. [9], this was attributed by the addition of PP copolymer in PA6 matrix result in improvement of impact strength as PP's impact strength was higher than PA6. The results also show that the incorporation of POE-g into all blends increased the impact strength of pure blends. Interestingly to note that PA6/PP (70:30) blends reached maximum impact strength with the incorporation of 10wt% POE-g which is more than twice higher than toughened PA6 and nearly twice higher than toughened PP. Similar observation was reported by Holsi-Miettinen et al. and Montiel et al.[2], higher impact strength was obtained for SEBS-g and EPR-g or SEBS-g toughened PAPP respectively where PA phase was dominant. The reason was reported that the addition of PP probably activating some other toughening mechanism that improved the impact strength of PA6/PP blends than toughened PA [Holsi-Miettinen et al]. As suggested by Tjong [], the highest impact strength of PP-PA (20:80) among other PP-PA blends was attributed by debonding and cavitation occur simultaneously at the PP-PA interface, which promote massive shear deformation in the PA matrix thus increase the amount of energy being absorbed. However addition of organoclay reduced the impact strength of toughened PA6, PP and PA6/PP blends. For the nanocomposites, the impact strength of PA6/PP (70:30) blend was the highest, similar to that of toughened PA6/PP (70:30) blend. These results indicate that in terms of toughness,

PA6/PP (70:30) is the optimum weight fraction for POE-g toughened PA6/PP and toughened PA6/PP nanocomposites.

Phase morphology

Figure 4 (a) (b) and 5 (a) (b) show SEM micrographs of freeze-fractured surfaces under liquid nitrogen of PA6PP (8:2) blends, PA6PP (6:4) blends respectively. The etched surfaces showed dark circular holes which represent the POE particles as heptane dissolved only rubber phase but not dissolve the PA6 or PP. Figure 4 show particles size of POE-g in PA6PP (8:2)(a) blends smaller than POE-g particles size in PA6PP (6:4) blends. This reveals good compatibility between PA6PP and POE-g rubber in PA6 major component as a result of interaction between maleic anhydride group of POE-g and PA6.

Similar observation found on the particles size of POE-g in PA6PP nanocomposites. POE-g droplets size increased with increasing weight fraction of PP. However it was observed that the POE-g size in PA6PP nanocomposites was smaller than PA6PP blends. For example the POE-g range particles size drop from 0.31-6.8 in PA6PP (6:4) (figure 4 (b)) blends to 0.15- 5.4 (figure 5 (b)) in PA6PP nanocomposites blends at the same composition. Khatua et al [10] were reported similar observation in the case of PA6/EPR nanocomposites where domain size of EPR decreased even when small amount (~1wt%) of organoclay added. These might be attributed by the changes in rheological properties and barrier effect for preventing coalescence of dispersed phase. For that reason addition of organoclay reduced particles size of POE-g dispersed as a result of organoclay act as a barrier to prevent coalescence.

CONCLUSION

The mechanical behaviour of PA6PP, toughened PA6PP and toughened PA6PP nanocomposites depends on the propotion of the constituents. The flexural strength and flexural modulus of the PA6PP decreased with the incorporation of POE-g. The reduction is most significant for PP dominant system. Incorporation of organoclay with the present of POE-g leads to the enhancement in flexural strength and modulus but expense the toughness of toughened PA6PP. Blends of PA6PP with 7:3 showed the maximum impact strength for both toughened blends and nanocomposites. SEM observation on the cryogenic surface revealed that the POE-g particles size were decreased with incorporation of organoclay and finer dispersion found in PA6 dominant blends systems for PA6PP and PA6PP nanocomposites.

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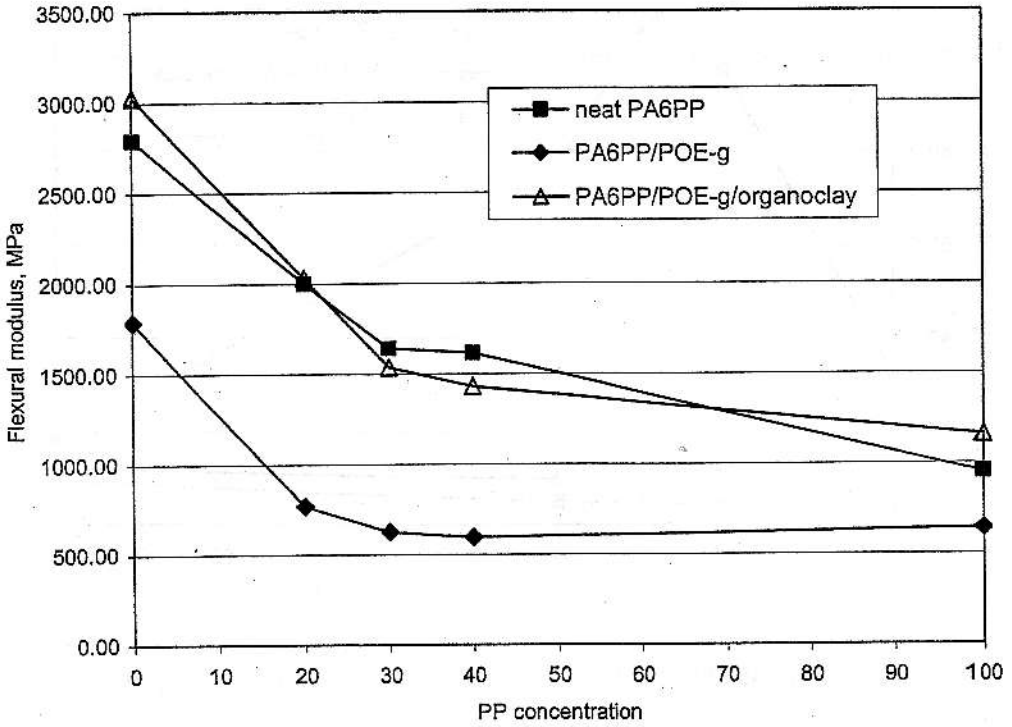


Figure 1: The effect of PA6PP blend ratio on flexural modulus

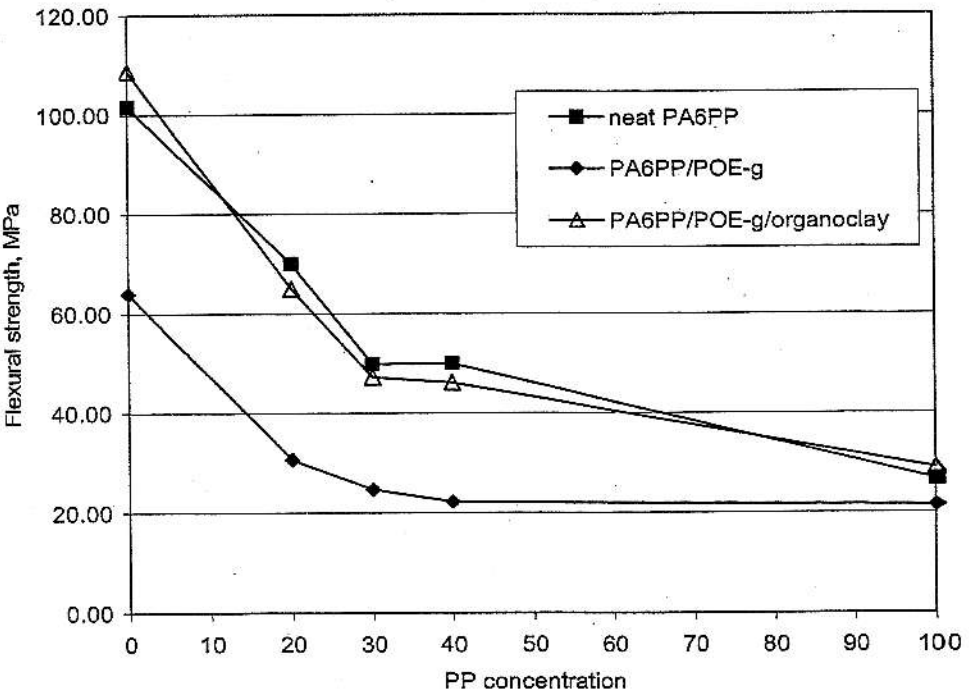


Figure 2: The effect of PA6PP blend ratio on flexural strength

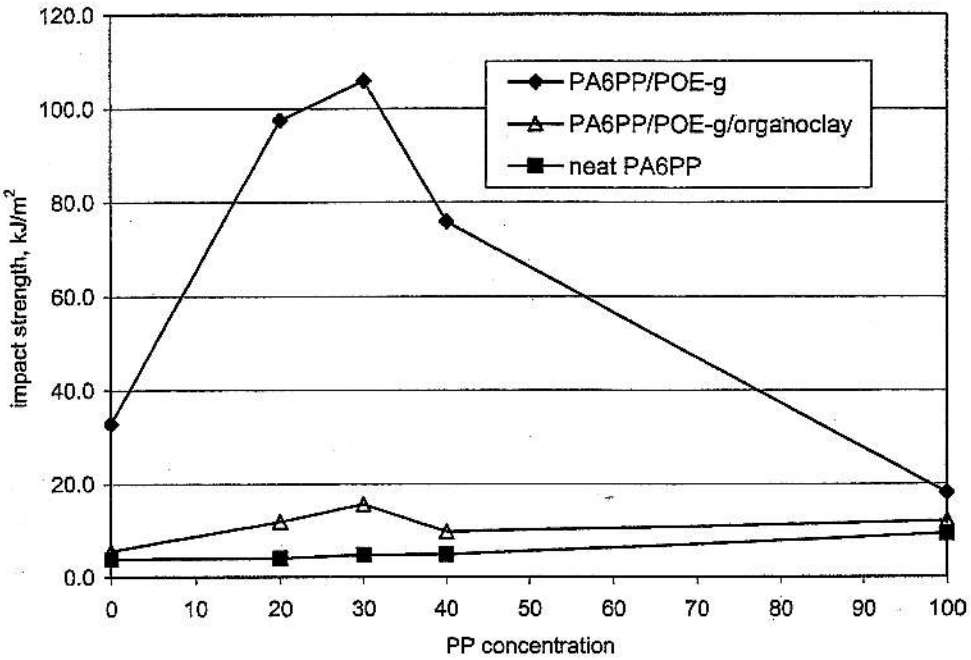
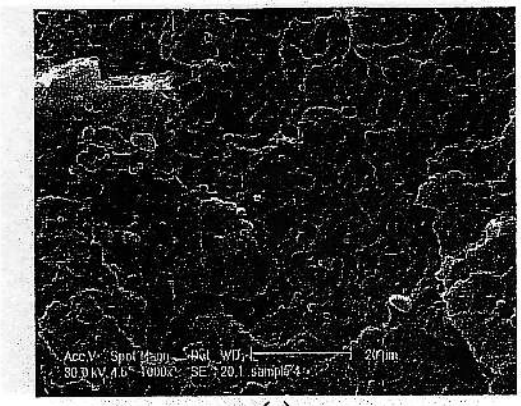
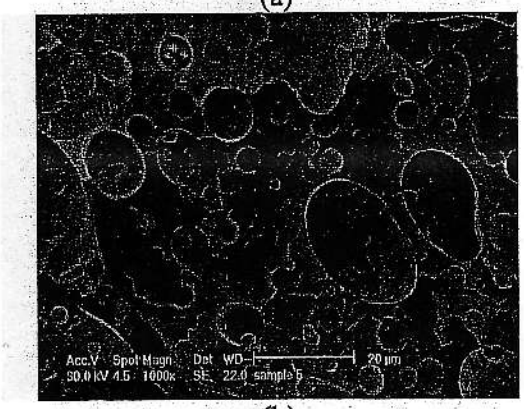


Figure 3: The effect of PA6PP blend ratio on impact strength

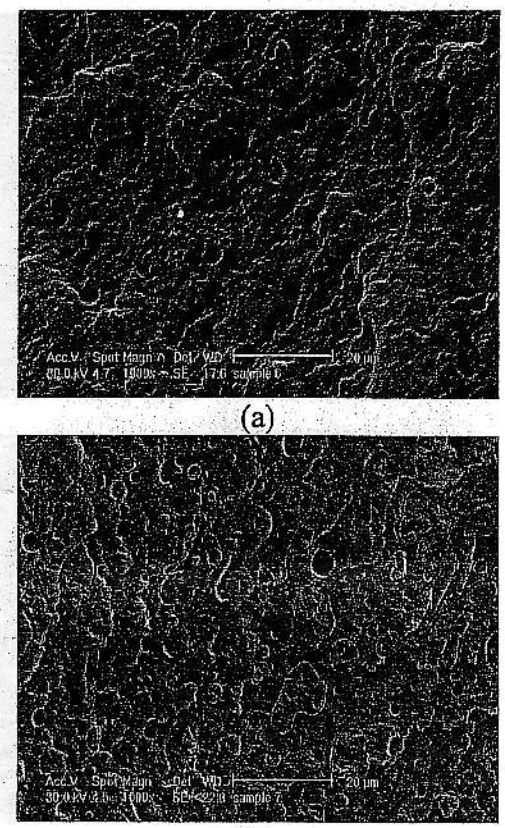


(a)



(b)

Figure 4: SEM micrographs of cryo-fractured surfaces extracted by heptane (a) PA6PP (8:2)/POE-g (b) PA6PP (6:4)/POE-g



(a)

(b)

Figure 5: SEM micrographs of cryo-fractured surfaces extracted by heptane (a) PA6PP (8:2)/POE-g/organoclay (b) PA6PP (6:4)/POE-g/organoclay